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OPTICAL DETECTION OF MAGNETIC RESONANCE IN SEMICONDUCTORS.(U)

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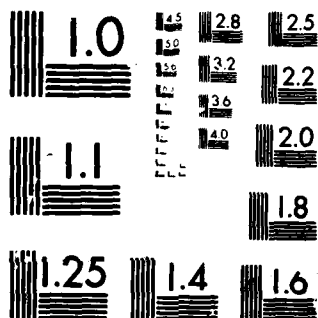
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The report describes modifications to an ODMR spectrometer and application to trapped excitons in CdTe. A technique of measuring EPR via the photo-induced conductivity is described and novel results of the application to GaAs:Cr are discussed.		

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Optical Detection of Magnetic Resonance in Semiconductors

by

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Abstract

This report describes work on compound semiconductors using spin sensitive optical polarization and photoconductivity. Since the grant was awarded in February 1979 the spectrometer has been redesigned to give greater versatility and sensitivity. Some of the design features have been implemented and tested to show that theoretical advantages are indeed matched by experiment. The experiments so far attempted have been concerned with CdTe and GaAs:Cr. For CdTe, recombination luminescence following band gap excitation has been shown to be due to recombination processes involving donor states with $g_D = 1.61$ and acceptors of $g_A = 1.35$. The spectral dependence of these resonances show that the recombination is complex involving excitons trapped at neutral donors and neutral acceptors as well as holes trapped at neutral donors. The advantage of applying spin sensitive photoconductivity is readily apparent in experiments using band gap excitation in CdTe. When used for semi-insulating GaAs:Cr one remarkably observes the 5T_2 ground state resonance even when excited with photons of energy less than one half the band gap energy. In fact spectral dependence of this resonance shows most of the sharp vibronic features of the ${}^5T_2 + {}^5A_2$ absorption band.



1. Research Objectives

Our interests have been to study transport phenomena in various materials using techniques of spin dependent polarized luminescence and photoconductivity. To make this possible has required upgrading the basic spectroscopy already available in T.C.D. very appreciably, both in terms of sensitivity and functional versatility. The various modifications planned, and installed are outlined in §3. So far we have tested the instrumentation on a range of semiconductor materials including GaAs:Cr, GaSe:S, Si:SiO₂ wafers, CdTe and amorphous Si. Basically we aim to identify the charge carriers which can be photo-excited and measure their properties (g-values, effective mass etc.).

2. Research Personnel

The following persons have worked on various aspects of the programme:-

Professor B. Henderson	- principal investigator
Dr. D. C. O'Connell	
Mr. J. Bolton	- research student
Mrs. C. McGilp	- research student
Mrs. N. Kelso	- secretary

3. Instrumentation

Basically two related but quite different techniques are being developed.

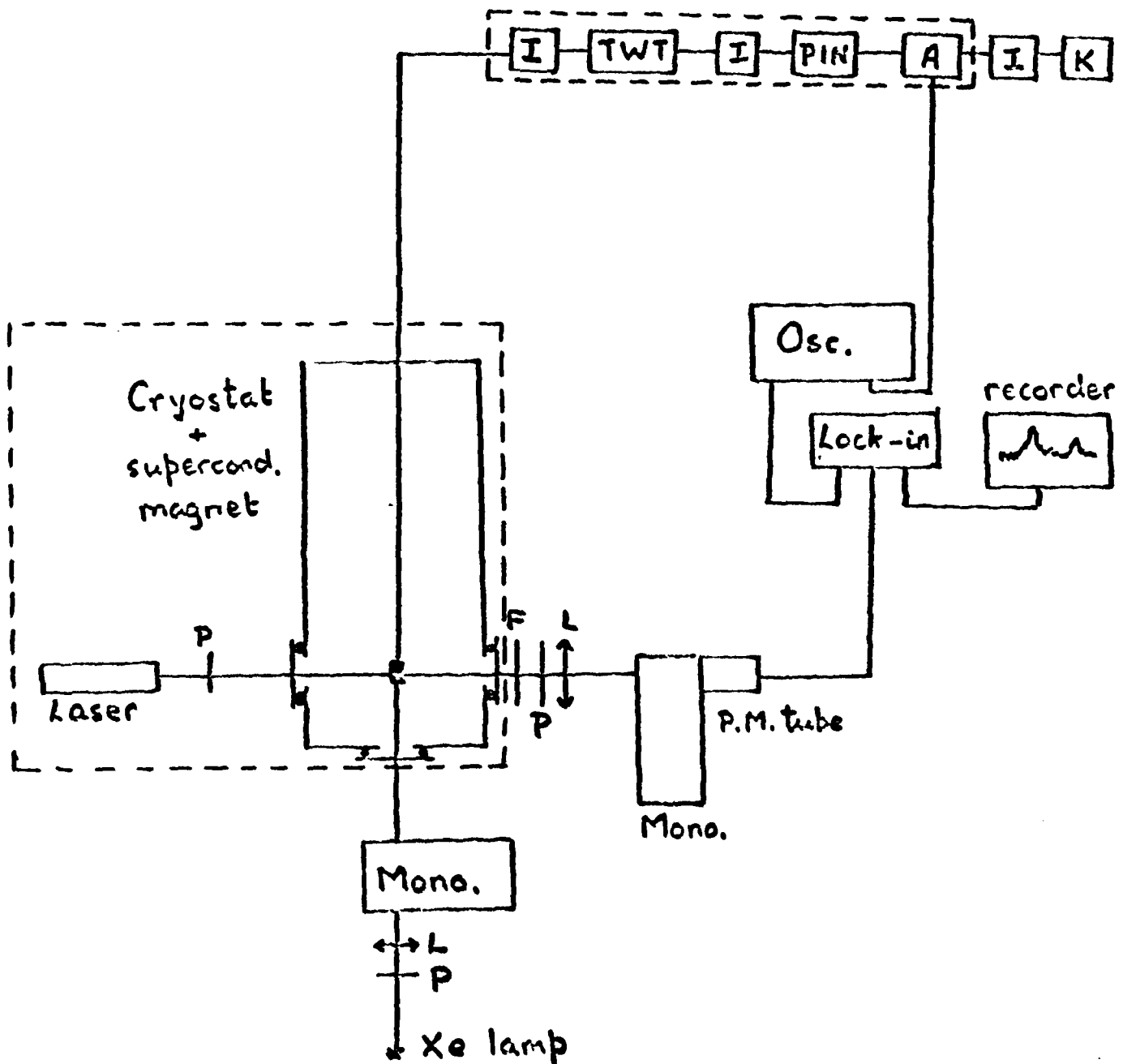
(a) Optical Detection of Magnetic Resonance (ODMR)

The instrumentation is shown in Fig. 1. The microwave arrangement

Figure 1: Schematic representation of ODMR spectrometer.

Key:

- K - klystron
- I - 30 dB isolator
- A - 40 dB precision attenuator
- PIN - PIN modulator
- TWT - travelling wave tube
- P - polarizer
- F - filter
- L - lens



has been designed to give maximum flexibility, and to avoid the very expensive replacement of low noise klystrons. Thus we aim to have a microwave system which will operate in the range 8-18 GHz, using the newest range of broad band, coaxially coupled microwave components. In the figure I indicates a 40 dB isolator, P - PIN modulator for 100% modulation of the microwave, A - 40 dB attenuator and T is a travelling wave amplifier which will give an amplification of up to 18 Watts. With this arrangement we can work with amplitude modulated microwaves at power in the range 10 mW to 18 W. We have chosen two microwave sources both cheap, low cost Gunn diodes one operating at 9.5 GHz and the other at 18 GHz. The broad band components are not cheap, although the Gunn diodes are as cheap as \$20. The changed arrangements, relative to those used in the last report are shown by the broken lines in Fig. 1.

Modifications have also been made to the magnet and optical system. The conventional Varian 9" electromagnet has now been replaced by a 6.5 Tesla superconducting magnet. An advantage of optically detected EPR is that by variation of the excitation wavelength or luminescence wavelength one can identify a particular EPR with the optical absorption/luminescence characteristics of the crystal. Hence we have installed two alternative sources, one a broad band 500 W Xe lamp and 0.75 m monochromator, the other a 6 W Ar^+ laser. The detection is via a 1 m grating monochromator, GaAs phototube and lock-in amplifier.

(b) Spin Sensitive Photoconductivity (SSPC)

The ODMR system described above is easily modified to incorporate leads to allow measurement of the variation in photocurrent at electron resonance. This allows direct correlation of charge carrier properties, during donor-acceptor recombination.

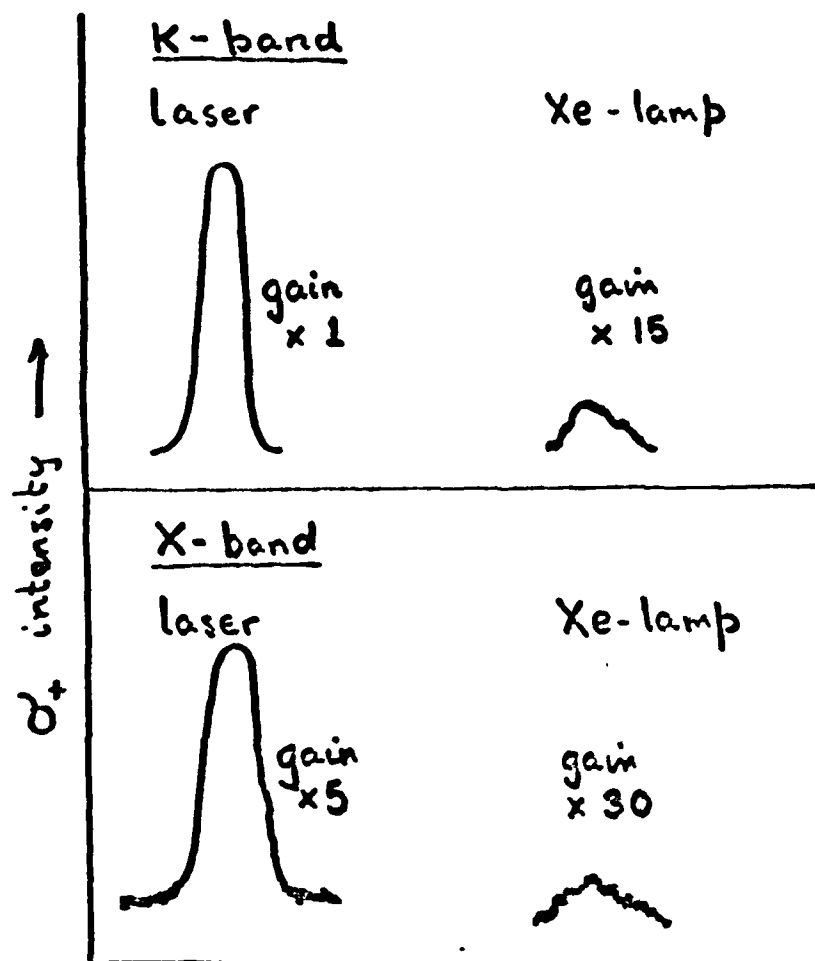


Figure 2: Effect of experimental variables on ODMR intensity of F_A centre in CaO . The microwave power has been maintained at 50 mW for both x-band and K-band. Measurement temperature is 1.6 K.

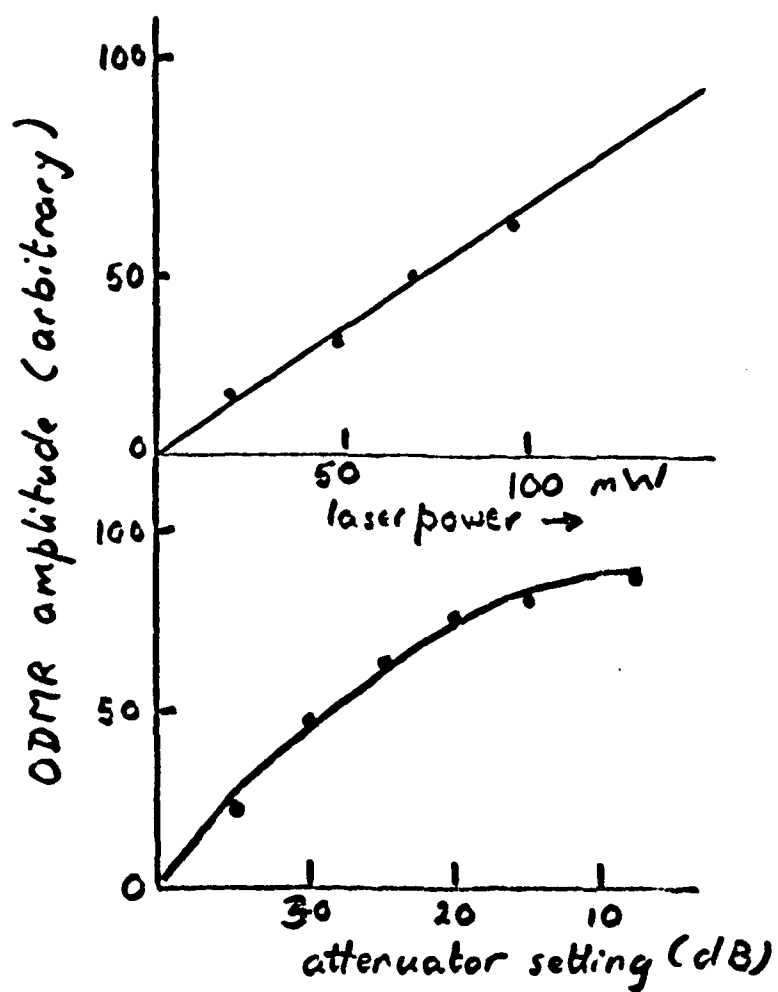


Figure 3: Variation of ODMR intensity with a laser pump power and microwave power.

4. Operational Improvements

It is important to remember that in ODMR one is detecting the optical photon rather than the microwave photon. Accordingly the signal:to:noise ratio is given by

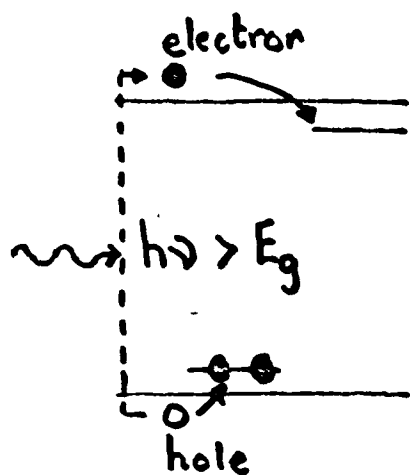
$$\sigma = (\alpha^2 n \eta E / \tau_R)^{\frac{1}{2}}$$

where α is a coefficient representing the fractional population change in the total population, n of the emitting levels at magnetic resonance, which consequently depends on the population difference of the spin multiplet and the degree of saturation. η/τ_R is the number of photons emitted per unit time in the luminescence line and η is the fraction incident on the phototube, and E is the photodetector efficiency. Hence we can improve the resonance signal mainly through α , n and η . This latter factor η is geometrical quantity which is in general improved for laser excitation relative to a broad band lamp. Typically for a laser $\eta \sim 10^{-1}$ whereas for broad band sources $\eta \sim 10^{-3}$ or worse. Of course the ability to maintain a steady excited state population is greatly improved for laser excitation also. α is determined mainly through the microwave pumping action hence it depends on frequency and power of the microwave pump source. Some typical results for the F_A centre in CaO are shown in Fig. 2 and 3. The clear advantage in using laser excitation and being able to vary the microwave frequency and power is immediately obvious. The advantages of the versatile system shown in Fig. 1, not all of which has been implemented, thus are amply demonstrated.

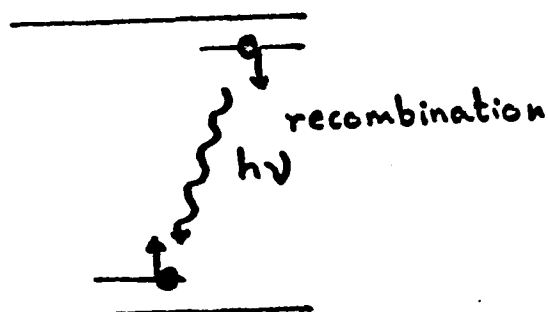
5. ODMR in Donor-Acceptor Recombinations

Consider the general case of recombination of an electron from a shallow donor with a hole on a deep acceptor (Fig. 4). Prior to

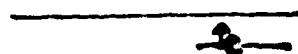
a)



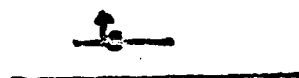
Either singlet



Or triplet



no recombination



b)

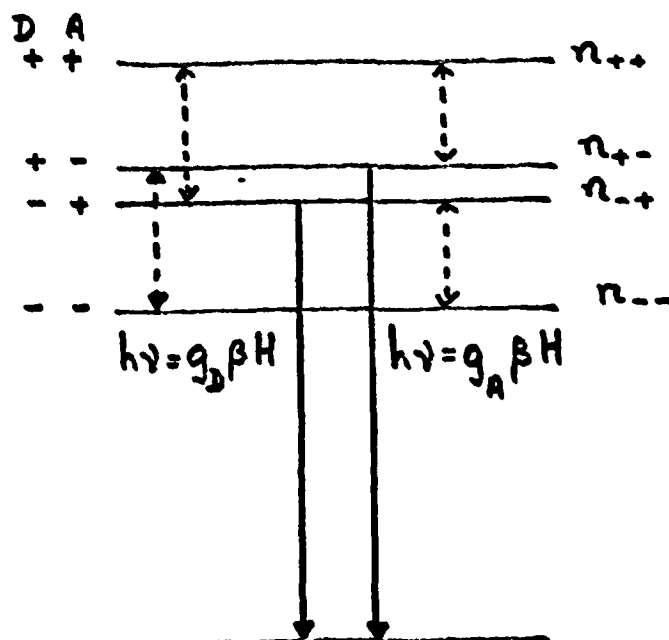


Figure 4: (a) Model of donor-acceptor recombination luminescence in semiconductors, and

(b) energy of donor-acceptor spin states in a magnetic field B .

excitation both donor and acceptor are non-magnetic so that the total ground state is a spin singlet ($S = 0$). Excitation creates an electron in the conduction band which is subsequently trapped on the shallow donor, and a 'hole' in the valence band which becomes trapped at the acceptor. Including spin the excited state of the pair is fourfold degenerate as shown. The strongly allowed selection rules for recombination conserve spin i.e. $\Delta S = 0$, where S is the total spin of the pair. The energy levels are just $E = \pm \frac{1}{2}(g_A \pm g_D)\beta B$, where g_A , g_D are the acceptor and donor g -values. The symbols $(++)$ etc. indicate the m_s value of donor and acceptor respectively. Hence the arrows joining the states $(--)\rightarrow(+--)$ and $(-+)\rightarrow(++)$ represent the two microwave induced donor resonances, which for very weak exchange coupling are degenerate. Similarly there are also two degenerate acceptor resonances.

Note that when the recombination lifetime, τ_R , is short relative to the spin-lattice relaxation time T_1 , the populations n_{++} and n_{--} build-up at the expense of the emitting n_{+-} , n_{-+} levels. Thus at resonance there is an increase in the recombination luminescence for both donor and acceptor EPR transitions. If however $T_1 < \tau_R$ thermal equilibrium is established between the excited states. Hence the microwave induced transitions may be observed only as a slight increase or decrease in total intensity for the donor or acceptor resonance.

Typical results are shown in Fig. 5 for CdTe (p-type) at 1.7 K and $\nu = 9.3$ GHz, resonances being observed with $g = 1.61$ and $g = 1.35$. The spectral dependence of the $g = 1.61$ resonance shows that three different luminescence lines give an identical optically detected EPR signal. These lines have previously been assigned to excitons recombining at neutral acceptors ($A^0 - x$) or neutral donors ($D^0 - x$) or holes recombining at a neutral donor ($D^0 - h$). Note that the intensity change at

resonance is of the order of 2% of the total light, far in excess of that expected for a spin multiplet in thermal equilibrium. Thus this resonance is identified as the electron (donor) resonance whereas the $g = 1.35$ resonance appears only on the $A^0 - x$ line and is identified as the hole resonance. Thus we find

$$\begin{aligned} |g_D| &= 1.61 \\ \text{and} \quad |g_A| &= 1.35 \end{aligned}$$

These assignments are confirmed by use of the spin sensitive photoconductivity which are discussed below.

6. Spin-Sensitive Photoconductivity in CdTe and GaAs:Cr

This is an extremely sensitive technique for measuring the ESR of electrons in the conduction band and holes in the valence band produced by band gap excitation. Such photoexcitation produces equal populations of electrons and holes. Now electron-hole recombination must occur via spin conserving selection rules. Hence the allowed recombination path is from an excited state in which the spins of electrons and holes are aligned antiparallel. The recombination rate, R , is just given by

$$R = P_s \omega_s$$

where P_s is the probability that the singlet state is occupied and ω_s is the singlet recombination rate. Since the spin state $S = 1$ is three-fold degenerate so that the triplet-state population $n_T \propto \frac{3}{4}$ and $n_s \propto \frac{1}{4}$. Since R is determined by n_s , any change in photocurrent is also determined by n_s because of the spin conserving selection rule. In fact in a magnetic field there are finite spin polarizations for electrons, P_e , and holes, P_h . Hence the singlet state probability is given by

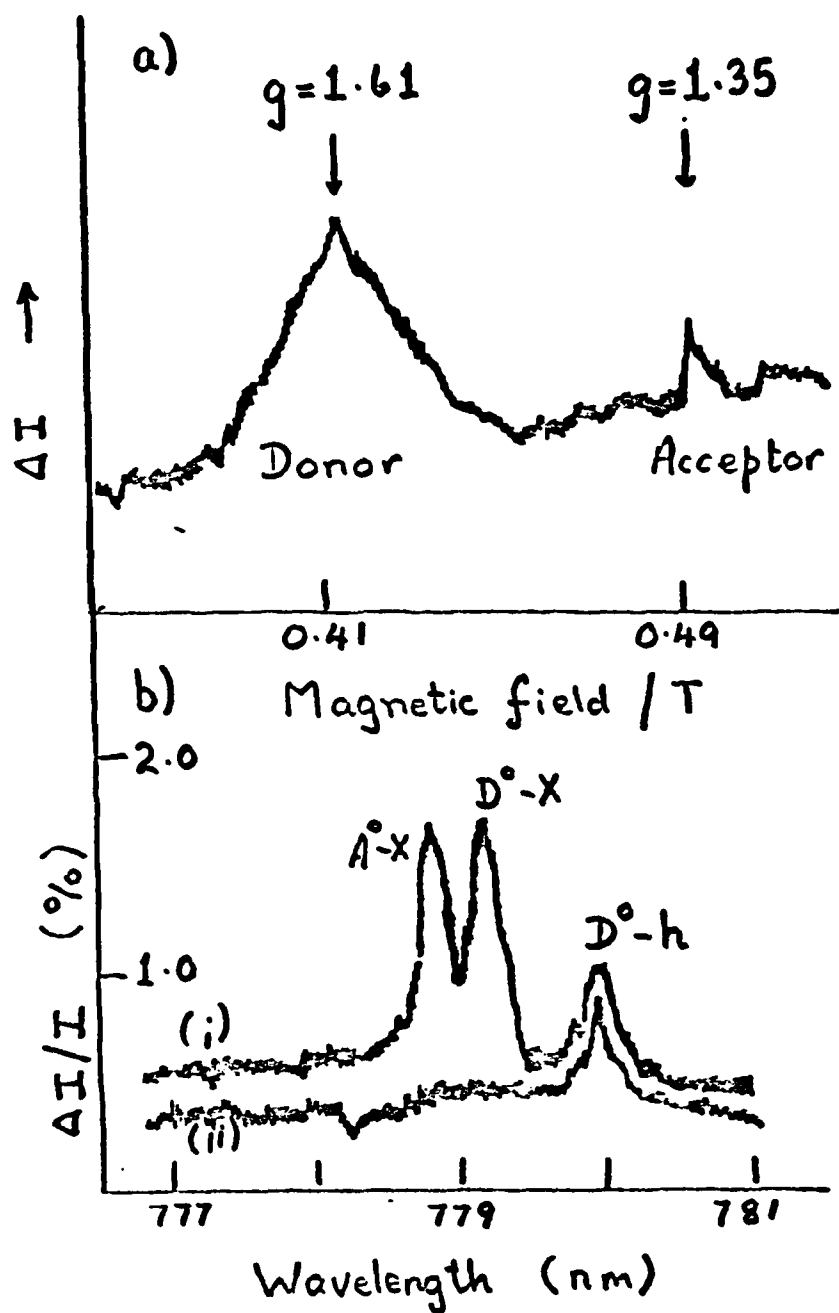


Figure 5: ODMR of CdTe at x-band and 1.2 K. In a) the donor and acceptor resonances are shown and their spectral dependences are shown in b).

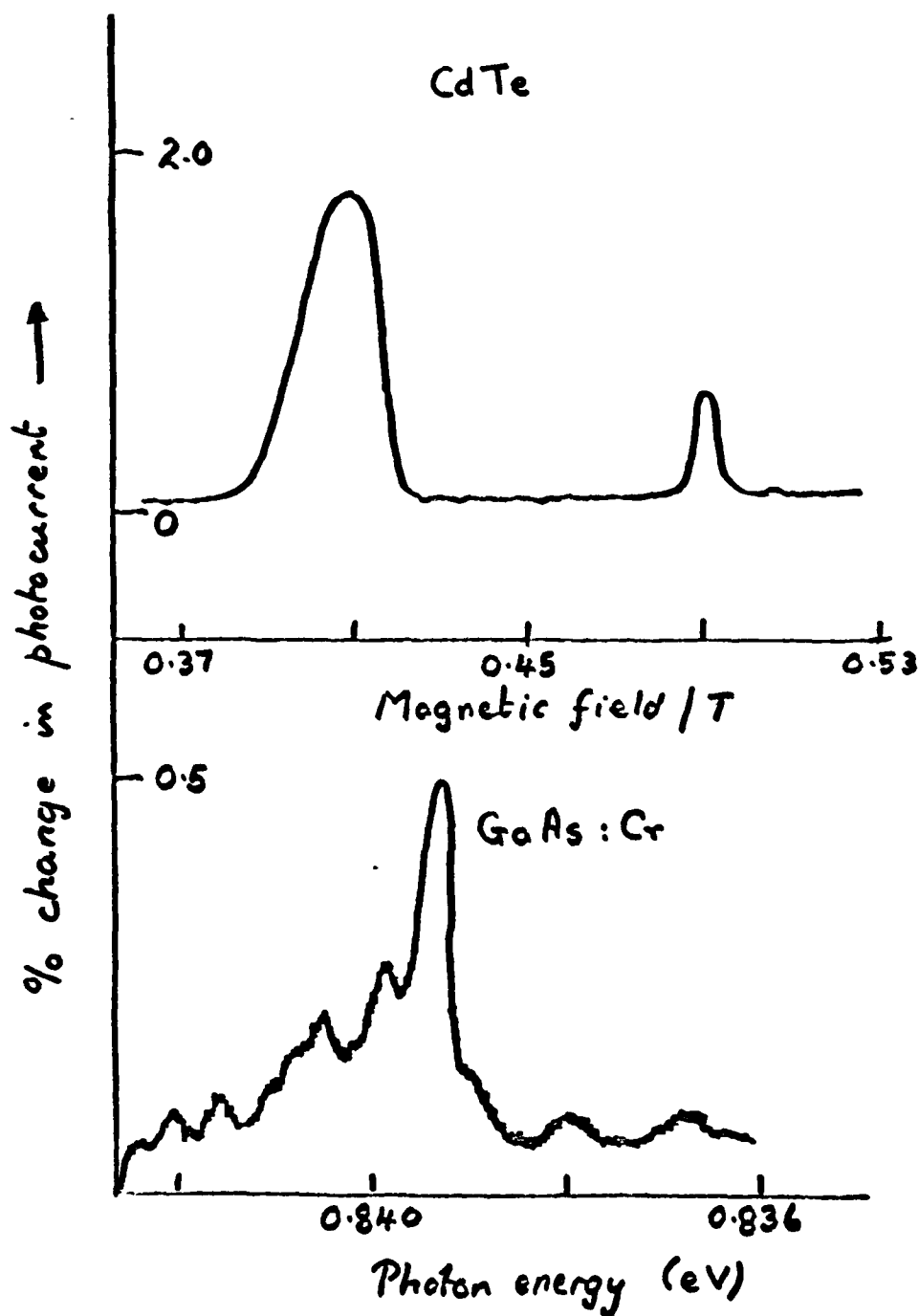


Figure 6: Spin sensitive photoconductive resonance in CdTe and GaAs:Cr.

In a) donor and acceptor resonances are shown at $g_D = 1.61$ and $g_A = 1.35$. b) depicts the spectral dependence of the Cr^{2+} ground state resonance in GaAs:Cr as the exciting wavelength is varied.

$$P_s = \frac{1}{4}(1 - P_e P_h) \quad \text{and}$$

$$R = \frac{1}{4}(1 - P_e P_h)\omega_s$$

Typically for a field $B = 0.3T$ and $T = 300 K$, $P_e \sim P_h \sim 10^{-3}$ so that the maximum change in R due to microwave induced changes in the spin polarization is of order 10^{-6} or $10^{-4}\%$. In amorphous Si a much bigger effect is observed experimentally: this arises because of the distribution of close donor/acceptor pairs.

Assuming the model in Fig. 4, there are n_o donor-acceptor pairs, n_s are converted to singlet states and n_T to triplet states. If g is the total rate of pair population, proportional to the pump intensity then

$$g_s + g_T = g \quad \text{and} \quad g_T = 3g_s$$

The dynamic pumping situation is determined by the rate equations

$$\dot{n}_s = g_s(n_o - n_s - n_T) - (\omega_s + \omega_D)n_s$$

$$\dot{n}_T = g_T(n_o - n_s - n_T) - (\omega_T + \omega_D)n_T$$

where the ω 's are transition rates for singlets, triplets and for dissociation. Under strong optical pumping the number of empty pair sites is zero

$$\text{i.e.} \quad n_o - n_s - n_T = 0$$

and the solution of the rate equation gives

$$R = \frac{\omega_D}{4\omega_D + 3\omega_s} \times \omega_s$$

The significance of this equation is that in the absence of dissociation (i.e. $\omega_D = 0$) there can be no recombination because all pairs exist as triplets. However the efficiency of recombination can be restored by promoting microwave transitions (EPR) at the donor or acceptor. In fact the fast EPR transitions between spin states will partially restore the $S = 0$ and $S = 1$ distributions. Thus the photocurrent changes at fields

corresponding to the electron/hole resonance. These changes can be as much as 1%, and so is easily detected.

Fig. 6 shows the SSPC resonance observed at x-band in CdTe with $T = 77$ K and using band gap excitation. The change in photocurrent is 1.5% at the resonance field, which corresponds to $g = 1.67$. This closely corresponds with the g -values observed for donors using the ODMR technique. Also shown is the spectral dependence of the optically detected ground state resonance of Cr^{2+} in GaAs. This shows many of the vibronic interactions of the absorption band of the ${}^5\text{T}_2 \rightarrow {}^5\text{A}_2$ transition observed in semi-insulating GaAs:Cr. However it is emphasized that in this case band gap excitation is not being used. Instead the photoconductive resonance is produced by pumping with a tunable colour centre laser, an F_2^+ centre laser in NaCl, the tuning range of which is from 1.35μ to 1.60μ . This particular resonance is rather difficult to understand except in terms of either two phonon absorption processes giving band-band excitation or photoionization from the Cr^{2+} ground state into the conduction band. A great deal of further work requires to be done to understand both the SSPC resonances shown in Fig. 6. The major point here is the very great sensitivity of the method - in the case of GaAs:Cr the resonance was not observed by ODMR and yet is clearly apparent in the SSPC resonance experiment.